

A High-Resolution, Multipass Time-of-Flight Mass Spectrometer for Investigation of Elemental, Isotopic and Molecular Compositions. G. P. Miller¹, J. H. Waite¹ and D.T. Young¹. ¹Southwest Research Institute (Space Science Department Div. 15, 6220 Culebra Road, San Antonio, TX 78228 email: gmiller@swri.edu).

Introduction: We report on the development of a third-generation, small, rugged, high-resolution, high mass range, time-of-flight mass spectrometer utilizing a folded ion optical path. The instrument is suitable for the investigation of the elemental, isotopic and molecular compositions of planetary and cometary atmospheres, exospheres, ionospheres and the regolith. The instrument is fitted with a high sensitivity electron impact source with high duty cycle producing classical electron impact mass spectra. Data obtained from the early prototype instrument originally proposed for the Mars Science Laboratory [1] was used to experimentally show the concept of folding the ion optics as a feasible means to minimize the length, volume and mass of the sensor. We further show that high resolution can be achieved while maintaining a small instrument form factor easily accommodated on a spacecraft or lander deck. In conjunction to the ion optical development, we have developed flight-like gas enrichment system to allow for the precise measurement of noble gas isotopes and methane. A specially designed two-stage time-of-flight detector is employed to handle the large dynamic range of measurements expected as well as a 10 bit high speed 3 gigasample per-second analog to digital converter for data acquisition. Some measured data from these instruments is shown including data acquired after interfacing to a gas chromatograph. Also presented are alternate folded path instrument geometries being studied having potentially smaller footprint for missions where mass and volume are at a premium.

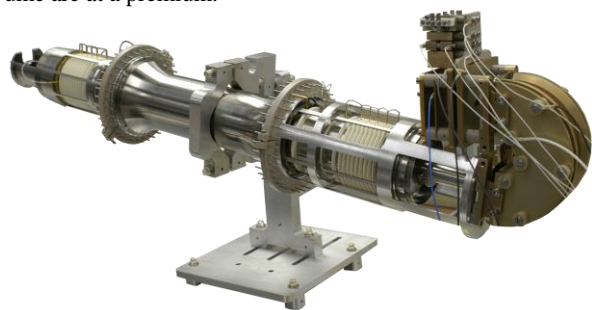


Figure 1 Second and third generation ruggedized multi-pass high-resolution time-of-flight mass spectrometer. This instrument is constructed out of titanium and ceramic allowing it to be baked at high temperature. The main structure of the instrument has been shaken up to 12 g_{rms}.

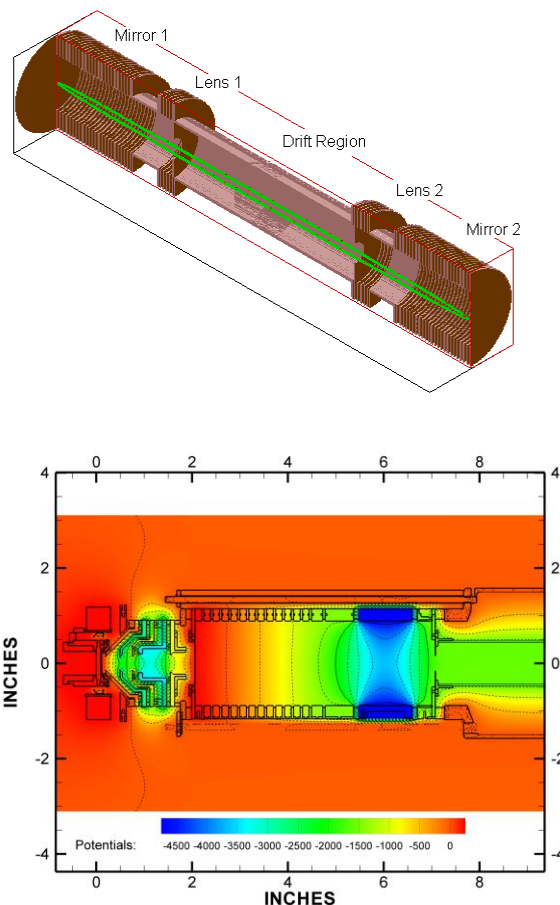


Figure 2 Simulated stable off-axis trapped ions paths between the mirrors are shown on the top along with the potential distributions along the length of one of the ion mirrors on the bottom.

Instrument Description: The multi-pass time-of-flight instrument consists of two gridless ion mirrors (reflectrons) in a coaxial arrangement separated by a field-free drift region (Fig. 2). The ion source is at one end and the detector on the opposite end. The coaxial arrangement does not require the use of deflection optics that would result in loss of resolution and added complexity, nor are grids employed to define the deceleration and reflex sections of the mirrors that would result in unacceptable transmission losses at the grid wires after multiple ion passes.

The spectrometer may be operated in linear mode (nominal mass resolution) or variable resolution (multi-pass mode). The former mode of operation is used to generate survey spectra while the later is employed for high mass resolution measurements to address potential mass interferences.

In operation, ions are injected in short bunches (typically a few nanoseconds wide) by the application a fast rise-time (about 5 ns) high voltage pulse to the extractor applied for typically between two or three microseconds in duration. A short, two-stage acceleration region defines the location of the first time focus and focusing elements within the ion source define the extent of the beam diameter. The extraction pulse defines the start of the time-of-flight measurement that ends when ions are registered at the detector. Ion mass/charge (M/q) is then given by the equation $M/q = 2U_0 t^2 L^{-2}$, where U_0 is the energy of the ions entering the spectrometer (defined by the extraction voltage pulse), L is the ion path length, and t is the measured time-of-flight. For ion injection into the coaxial mirrors, the voltage on the first ion mirror end plate is momentarily lowered below the extraction potential allowing the ion bunch to pass through the plate while the potential on the end plate of the second mirror is kept high. After a predefined time (typically 3-6 microseconds), the voltage is raised to trap the ions between the two mirrors. Ions trapped in the mirrors are allowed to execute the necessary number of laps to reach the required time dispersion of the mass ions of interest. After the predefined time for mass separation, the potential is dropped on the end plate of the second mirror allowing the ions to pass into the detector that registers their time-of-flight.

If while executing multiple passes the ion bunch does not disperse in time while being trapped within the mirrors, the resolution will increase in proportion to the length that the ions travel within the mass analyzer according to the relation: $M/\Delta M = t/2\Delta t = 2^{-3/2} (L/\Delta t)(M/U_0)^{1/2}$ Where; L is the distance that the ions have traveled, M is their mass, t is the time-of-flight as measured at the detector and U_0 is their energy.

Because resolution depends on the ratio of ion path length to TOF peak width, very high resolution is theoretically possible if $L/\Delta t$ can be made large, either by lengthening the ion path or shortening the mass peak width, or both. Lengthening the path can be accomplished either by making the spectrometer longer, which increases resource usage (i.e. pumping, mass), or by folding the ion flight path back on itself which forms the basis of our design. Decreasing the width Δt of the ion packet below a few nanoseconds in time is limited by a number of factors too difficult to overcome in practice using gaseous ion sources, current state-of-the art high speed electronics and detector technology.

Ion Storage Source: Since most of the sensitivity originates with the efficiency of the ion source, we have designed and constructed a high sensitivity storage ion source based on the work of R. Grix et al. [2]. The ion source is designed to ionize, store and pulse ions out for mass analysis at repetition rates up to 10 kHz with up to 1×10^5 ions per extraction. The ionization is accomplished across a long ionization path length where the formed ions are trapped in a shallow potential well created by the space charge of the ionizing electron beam [Fig. 3.]. The high duty cycle improvement of the mass spectrometer comes from the fact that after extraction and during mass analysis, the time between extractions is not wasted but rather used to ionize and store ions in the potential well for the next extraction event. This ion accumulation (storage) between extractions results in high duty cycle and

enhancement in sensitivity needed for precise measurement of low abundance species.

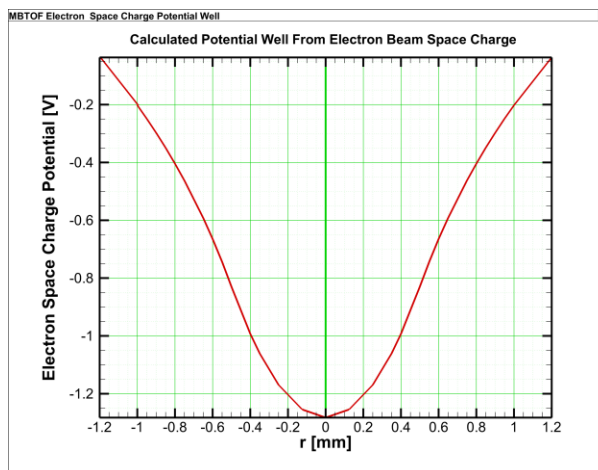


Figure 3 Calculated electron beam source potential depression. Ions are stored in this well between ion extractions.

Results: Shown below are some examples of the performance of the mass spectrometer in both linear and multi-pass mode of operation using gas leaks and a gas chromatograph interfaced via a heated transfer line. They demonstrate the high mass resolution measurement of various mass doublets of interest that require higher than nominal mass resolution to separate and quantify and isotope abundance measurements free of interfering mass peak tails

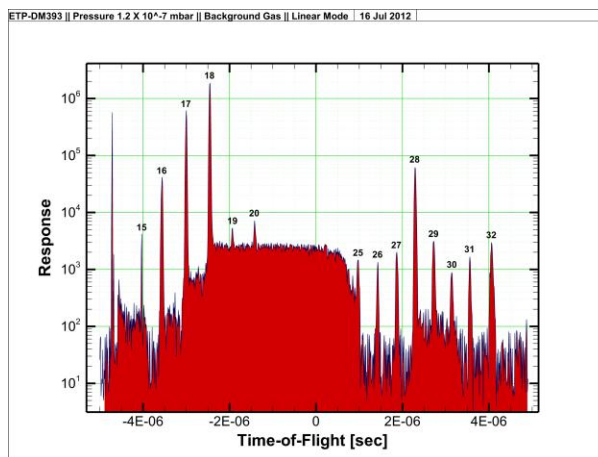


Figure 4 Spectra taken with high dynamic range TOF detector in linear mode using background gas.

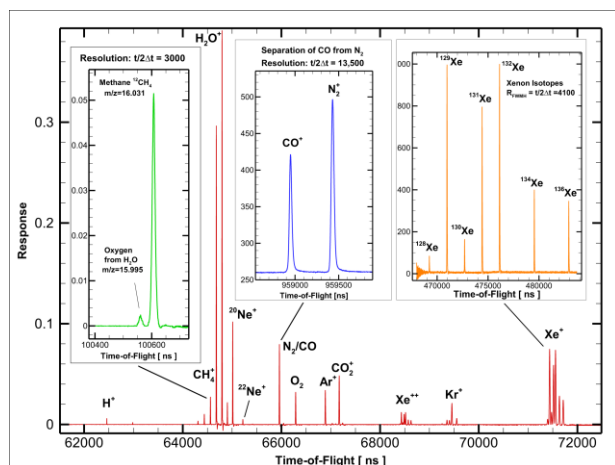


Figure 5 Linear-mode spectra shown in the lower trace in red for a mixture of compounds of interest. Inset boxes are spectra at high mass resolution (multi-bounce mode) for mass doublets of interest.

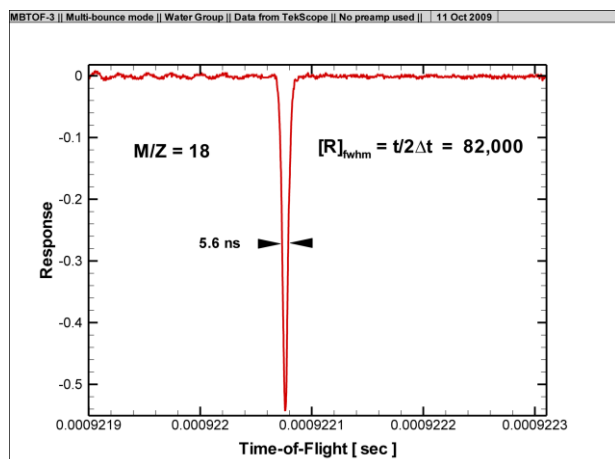


Figure 6 Example of a very high resolution mass spectrum acquired at mass 18 after nearly a milli-second of flight time between the ion mirrors.

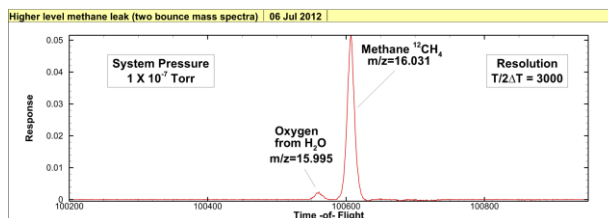
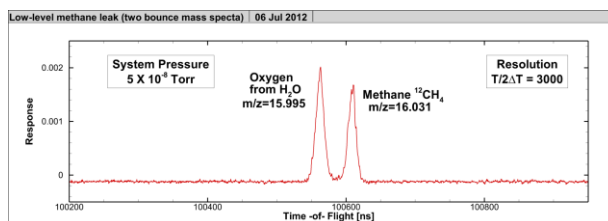


Figure 7 Resolving methane from oxygen (nominal mass 16) from background water after several passes through the analyzer.

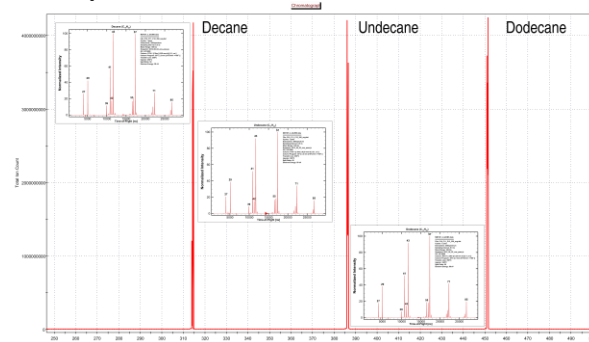


Figure 8 Gas chromatograph (total ion current) and mass spectra of a three-component hydrocarbon mix acquired at a 10 kHz extraction rate. Spectral skew normally seen on scanning-type mass spectrometers when peaks elute from the column is not observed in a TOF mass spectrometer.

Conclusions: We have demonstrated that high resolution and sensitivity can be attained with a small mass spectrometer having a folded ion optical path. Combined with a highly efficient electron impact (EI) storage ion source, the instrument generates classical EI mass spectra for the determination of elemental, isotopic and molecular compositions.

References:

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- [2.] R. Grix, U. Gruner, G. Li, H. Stroh, H. Wollnik, An electron impact storage ion source for time-of-flight mass spectrometers, International Journal of Mass Spectrometry and Ion Processes, Volume 93, Issue 3, 10 October 1989, Pages 323-330, ISSN 0168-1176, 10.1016/0168-1176(89)80121-1.